Diagnostic Characterization of High-Power Lithium-Ion Batteries For Use in Hybrid Electric Vehicles

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Introduction

Lithium-ion batteries are a fast-growing technology that is attractive for use in portable electronics and electric vehicles due to their relatively high specific energy and specific power. The Advanced Technology Development (ATD) Program is a new effort by the U.S. Department of Energy (DOE) to aid the development of lithium-ion batteries for hybrid electric vehicle (HEV) applications. The ATD Program is a joint effort of five DOE National Laboratories: ANL, SNL, INEEL, BNL and LBNL. A baseline cell chemistry was identified as a carbon anode (negative electrode), a $LiNi_{0.8}Co_{0.2}O_2$ cathode (positive electrode), and DEC-EC-$LiPF_6$ electrolyte. Various diagnostic techniques were applied to determine cell component chemical, structural and morphological changes that lead to performance degradation and failure as they are aged, cycled and/or abused. These diagnostic results can be used to guide the improvement of cell chemistries. A full report of our results is available in Ref. [1].

Nine ATD baseline cells were fabricated by PolyStor, Inc. according to a design provided by ANL and tested at INEEL, ANL and SNL. These cells were not optimized, and were used only in studies of cell components under high-power battery simulations. High-current pulse profiles were generated specifically for performance characterization of these batteries in HEV applications in contrast to the constant-current profiles typically used in the characterization of lithium-ion batteries for portable devices [2]. Cells were opened (with care) in a helium-atmosphere dry box, followed immediately by diagnostics.

Ex-situ IR microscopy was conducted using a Nicolet Magna 760 with Nic-Plan IR Microscope in the LBNL Advanced Light Source. A synchrotron beam was employed due to its high brightness and small spot size (~ 10 μm), which provides good spatial resolution and allows detailed examination of the uniformity of the SEI on electrodes. Airtight IR cells with KBr windows were constructed to perform IR microscopy on the air-sensitive and moisture-sensitive electrode materials. Electrode samples were harvested from various locations on the electrodes inside a dry box and then inserted into the IR cells. At minimum, three spectra were recorded for each sample to ensure that our results were reproducible. The same set-up and reflectance geometry was employed for the IR measurements of electrolyte and other compounds such as propylene oxide on a glassy carbon substrate.

Results and Discussion

Anode. Typical IR spectra from different anodes are shown in Fig. 1. The anode samples from the virgin cell (Cell 1) were exposed to vacuum, and therefore no bulk solvent from the electrolyte remained on the electrode surface. As expected, the spectrum shows essentially no peaks characteristic of the electrolyte. A broad peak at 1650 cm^{-1} was observed, which is characteristic of C=O stretching of lithium alkylcarbonate, consistent with other literature

reports. [3] The peak at 838 cm^{-1} is strong, and is a characteristic feature of the SEI as discussed later. A similar IR spectrum was obtained for Cell 7 that was cycled at 60% SOC with a 3% SOC swing at $70^{o}C$ except that some electrolyte peaks were also observed because the sample was not evacuated. These results suggest that the SEI was formed during the formation cycles and remained even in cells that were subjected to 3% Δ SOC at temperatures as high as $70^{o}C$. No significant signals from Li_2CO_3 were observed in either IR or Raman measurements.
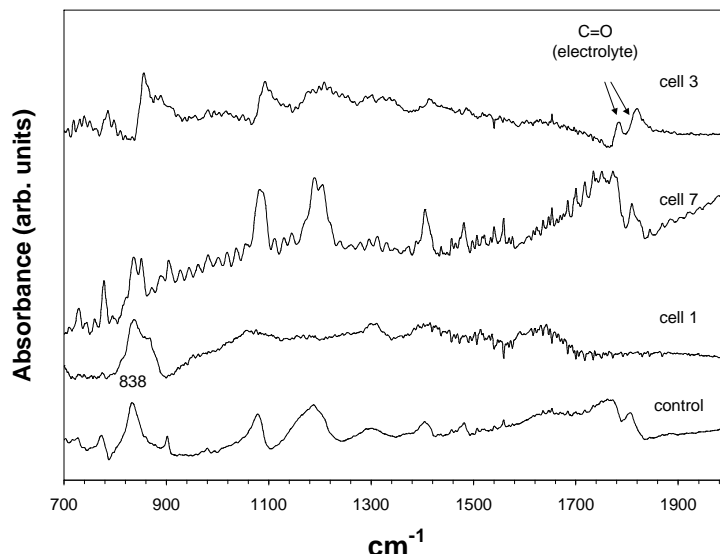

Figure 1. Typical IR spectra for the base line ATD cell anodes with cell number indicated, and for the controlled electrochemical experiment of reduction of LP-40 on a glassy carbon electrode.

To understand the role that the solvent (DEC and EC) plays in the formation of the SEI, electrochemical control experiments were performed in DEC/THF-LiClO$_4$ and EC/THF-LiClO$_4$ electrolyte. LiClO$_4$ was employed rather than LiPF$_6$ due to its relative stability against reduction. No significant SEI was detected by IR when DEC was employed. EC was found to be the key contributor to SEI formation, as shown in Fig. 2 b. The peak at 838 cm^{-1}, which was not seen in the electrolyte (Fig. 2 a), was observed again and appeared to be most intense of all peaks observed. It was ascribed by Aurbach et al to the bending mode of an organic carbonate group[4]. This SEI, however, shows a strong resemblance to propylene oxide (Fig. 2 c), which also has an intense vibrational peak at 838 cm^{-1} arising from C-O-C stretching of the epoxide ring. It is known that EC can be synthesized using ethylene oxide and CO_2[5]. A mechanism for the reverse reaction, i.e. EC decomposition to ethylene oxide or epoxide-containing material, however, is not available at this time.

The IR result was reproducible for each anode sample. Non-uniformity of the SEI layer was, however, observed for samples taken from different locations on anodes in tested cells. Only signals from the electrolyte were observed at some locations for a sample from Cell 3 in the inner side close to the current collector. This result is likely due to spatial variations of current density. If so, more current-collector strips could help to generate a more uniform SEI layer. The variation of pressure and temperature inside the cell could also play a role. Studies were carried out to investigate the cause(s) of this interesting phenomenon and its possible effects on cell performance.
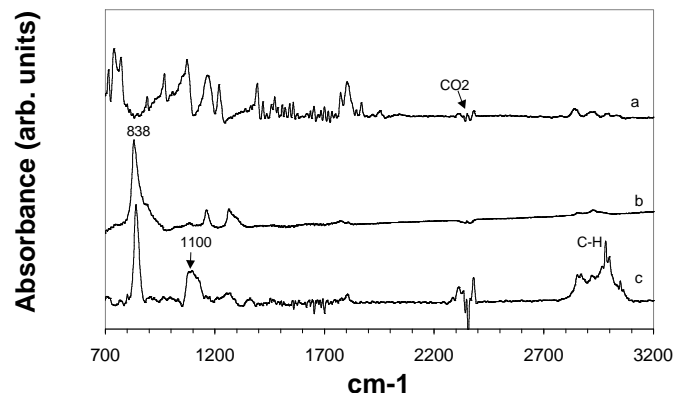

Figure 2. 4. IR spectra for a) the electrolyte EC/THF-LiClO4; b) SEI from reduction of the electrolyte EC/THF-LiClO4; c) propylene oxide.

Cathode. To gain additional insight into the nature of the nanocrystalline deposit that forms at the cathode at higher temperatures, we studied the structure and composition of the cathode surface

with Raman spectroscopy. Raman spectra of cathodes from Cells 1 (a) and 3 (b) are dominated by two strong and broad carbon bands at 1365 and 1580 cm^{-1} and a broad maximum centered around 500 cm^{-1}, characteristic for LiNi$_x$Co$_{1-x}$O$_2$ oxide. The large difference between the band intensities is mainly due to the much larger Raman cross-section of carbon compared to LiNi$_x$Co$_{1-x}$O$_2$, but is also due to a high concentration of carbon on the cathode surface. The C/LiNi$_x$Co$_{1-x}$O$_2$ peak ratio varied significantly between locations, suggesting a non-uniform surface concentration of cathode components. These observations were also confirmed by ESCA surface analysis.

Mid-IR (wave number range 600 – 4000 cm^{-1}) data revealed no observable SEI layer on the cathode surface, which suggests that the precipitate does not arise from oxidation of the electrolyte.

Conclusions

An SEI is formed on the anode surface during cell formation cycles, and no changes were detected by IR for a cell that was cycled at 3% ΔSOC and 70°C. The infrared spectroscopy of this surface layer showed a strong resemblance to that of propylene oxide. Non-uniformity of the SEI layer was, however, observed for samples taken from different locations on the anode in tested cells, which is likely due to spatial variations of current density. The SEI, however, deteriorated when cell was cycled at 9% ΔSOC and at elevated temperature. The impedance of cathode samples increased monotonically with temperature, however, IR spectroscopy detected no SEI on the cathode surface. The electrolyte compositions were analyzed via GC, and ethylene glycol was identified as a reaction product from the anode, which is consistent with the IR observation of the epoxide-containing material.   LiPF$_6$ salt was found to be unstable at elevated temperature and could also contribute to the cell performance decline.

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